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NISTIR 4788NIST
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April 1992



U.S. DEPARTMENT OF COMMERCE
Barbara Hackman Franklin, Secretary

TECHNOLOGY ADMINISTRATION
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**NATIONAL INSTITUTE OF STANDARDS
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ABSTRACT

The characterization of a polyurethane standard reference material, SRM 1480, is described. The weight-average molecular weight of SRM 1480 by light scattering was determined to be 4.7×10^4 g mole⁻¹. The intrinsic viscosity of SRM 1480 in THF was also measured and found to be 43.8 mL/g.

The Size Exclusion Chromatography (SEC) of SRM 1480 in THF as received in the bottle was found to exhibit concentration dependent peak positions, even at low concentrations. The addition of 0.01 moles per liter LiBr to the THF was found to alleviate this problem. This low concentration of LiBr did not change the Polystyrene calibration of the SEC columns.

1.0 Introduction

There is a growing need for better methods of characterizing the commercial polyurethanes used in medical devices, both before use and after degradation following implantation. Because of the wide variations in the compositions of these block copolymer systems, the usual methods for determining molecular weight distribution (MWD) are of limited applicability and are difficult to interpret. With support from the Food and Drug Administration (FDA) and the Standard Reference Materials Program (SRMP), we undertook a program to produce polyurethane Standard Reference Materials (SRMs) to develop improved methods for characterizing these and other block copolymer systems.

Two polyurethane SRM's, with weight-average molecular weights certified, and with limiting viscosity numbers determined under the conditions commonly used for the estimation of MWD by Size Exclusion Chromatography (SEC), had been originally envisioned for this program. This report describes extensive work on the low molecular weight Polyurethane SRM, SRM 1480.

2.0 Preparation of Low Molecular Weight Polyurethane Standard and Its Bottling

2.1. Preparation

The low molecular weight standard, SRM 1480, is not the usual commercial polyurethane, but rather is a model compound that could be treated as a homopolymer from the point of view of absolute molecular weight determination methods. The polymer was made by reacting a polyethylene glycol (PEG 600) with a narrow MWD and a purified diphenylmethane-4,4'-diisocyanate (MDI) (Dow Chemical Company designation xpr-270-0010-27-1).¹ This polymer has a well defined repeat unit as (MDI-PEG 600)_n. It thus could be treated as a homopolymer in either sedimentation or light scattering methods. This material differed from a normal polyurethane in that it had no chain extender.

The material was made at Dow Chemical, Connecticut, under the direction of Dr. Curtis Smith. The material, as received by us, was in the form of a gum.

2.2. Original Bottling

The material was given to Dr. R. McKenzie in SRMP for bottling. He used about 1/3 of the material that was received and bottled it in small bottles of about a gram of sample in each bottle. 331 samples were

¹Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards & Technology, nor does it imply necessarily the best available for the purpose.

bottled. The entire set of samples was divided into 20 subsets. One vial was randomly selected from each subset for homogeneity testing.

2.3 Homogeneity Testing on Original Bottling

Homogeneity testing was performed on samples of polyurethane taken from all 20 of the selected vials, with duplicate samples taken from 5 of the vials. The polyurethane samples were dissolved in tetrahydrofuran (THF) to form solutions of about 1.0 g/L concentration. The 20 solutions were compared by SEC using THF as the mobile phase. In this study a Waters 150-C ALC/GPC Liquid Chromatograph with a refractive index (RI) detector was used. Mallinckrodt THF was used as the solvent and a set of five Waters columns designated 10^2 , 10^3 , 10^4 , 10^5 and 10^6 A were used to separate the polymer.

From our SEC studies we found that this original material had a polystyrene equivalent molecular weight variation of as much as a factor of two from bottle to bottle. In fact some molecular weight variation was found within some of the bottles. Some chromatograms from these runs are shown in figure 1. The original material was then deemed too inhomogeneous to use as a SEC calibrant.

2.4 Dissolution of Remaining Material and Rebottling

It was decided to try to homogenize the polymer remaining from the original bottling by SRMP. After a number of solvents were tried, it was decided to dissolve the material in methylene chloride. A solution with about 35% polymer was made up. The solution, under an atmosphere of N_2 , was slowly rotated in a gallon bottle for three days. Then a volume of solution containing about 1.2 grams of solute was transferred into each of 324 numbered 15 mL bottles in the order of numbering. The bottles were put into vacuum ovens at about 40° C. A slow stream of dry N_2 was blown through the ovens overnight. The ovens were then pumped down to about one-quarter normal atmospheric pressure carefully watching that none of the polymer foamed over the edges of the bottles. After most of the methylene chloride had been removed from the bottles a vacuum was drawn (by continuous pumping) for 3 days. After the third day no additional material was found in the cold traps. The bottles were then filled with dry N_2 and capped. The possibility of photodegradation was minimized throughout the dissolution and rebottling process by shielding the polymer from the ambient light of the laboratory except when the polymer or its solution was being handled or observed.

2.5 Homogeneity Testing on New Bottling

324 samples were bottled. The entire set of samples was divided into 15 subsets. One vial was randomly selected from each subset for homogeneity testing. The weight of polymer in each of these 15 bottles was determined and found to be over 1 gram (1.1 to 1.3 grams). From each of these 15 bottles a solution of polymer in THF was made up for a SEC run.

The chromatograms from these runs superimpose on each other. Figure 2 shows some of these chromatograms. There was no way to distinguish one material from the other on the chromatogram except for some small difference at very low molecular weight where we also experience interference from additives to the solvent THF, Butyl-hydroxytoluene (BHT) or from any residual methylene chloride. Thus we consider that the rebottled material is homogeneous.

3.0 Limiting Viscosity Number of SRM 1480 in THF

The viscosity number as a function of concentration was obtained by making flow time measurements at 30 °C at concentrations of about 0.0025, 0.0050, and 0.0075 g/mL in tetrahydrofuran (THF). The viscometer used was a Cannon Ubbelohde semi-micro viscometer (Cannon # K 546). At least 0.1g sample of polyurethane was used to prepare each solution. The solvent was Mallinckrodt Tetrahydrofuran (stabilized) AR (Analytical Reagent). The solvent was used as received from the bottle. All solvents and solutions were filtered through BIO-RAD (catalog #343-0001) 0.45 μ m prep-disc membrane filters.

Two independently prepared solutions were run at each concentration. The viscosity number when fitted versus concentration appears linear to a concentration of at least 0.004 g/mL. On the basis of these results we estimated the limiting viscosity number of SRM 1480 to be 43.8 mL/g with a standard deviation of 0.17 mL/g. The Huggins constant was estimated as 0.431 with a standard deviation of 0.015. Table 1 gives the data used in the fit.

3.1 Measurement Scheme for Limiting Viscosity

Solutions were run in the capillary viscometer alternating with measurements of the solvent, THF, before and after each solution measurement. The concentrations were chosen in random order to provide the approximate desired distribution of concentrations over the whole series of experiments.

All three vertical tube members of the viscometer were rinsed with solvent from the top end down at the conclusion of the flow time determination for each solution. The sample injection tube and vent tube were rinse 6 to 8 times with about 2 mL solvent propelled from a syringe through a filter and a 22 gauge needle onto the glass surface inside the top end of the tube. The capillary tube was rinsed 4 times with about 5 mL of solvent injected into the top end of the tube. The solvent was propelled with a strong manual force from the syringe through a filter and a 22 gauge needle provided with a teflon tube section on it to connect the needle tip to the capillary tube.

The kinetic energy correction was determined on another viscometer of the same model and dimensions as the one used and was found to be essentially zero, using the method of Cannon, Manning and Bell [1].

3.2 Fitting Methods and Error Analysis for Systematic Error

Data were fit using a NIST viscometry program which uses a linear least squares fit of the flow times to a second order polynomial in concentration divided by solution density. From this fit the limiting viscosity number (LVN) and its standard deviation were estimated. A plot of the data is given in figure 3.

Since we shall not certify the intrinsic viscosity no effort was made to make a detailed systematic error analysis of this quantity. However from previous work using a similar viscometer, we estimate the systematic error limit to be about 2%.

4.0 Effort to Determine Molecular Weight Using Ultracentrifugation

An attempt to obtain the molecular weight of SRM 1480 was made using ultracentrifugation (UC). A Beckman Model E ultracentrifuge was used in this work. Dimethyl Acetamide (DMAC) was chosen as the solvent since it has little vapor pressure at room temperature. The first runs of the ultracentrifugation experiment at about 33 °C suggested that it would take more than 300 hours for the system to obtain an equilibrium concentration gradient. To decrease the time to obtain equilibrium the "over-speed under-speed" method of Richards-Teller-Schachman [2] was applied to the ultracentrifugation procedure for this solution system. Even with this improvement we could not establish equilibrium in the ultracentrifugation in less than 300 hours. Using this improved methodology, two preliminary runs were made on this polyurethane material at two concentrations.

These UC runs of SRM 1480 in DMAC showed a fringe displacement of 9.0 fringes for a concentration of 0.002 g/mL and 18.5 fringes for a concentration of 0.006 g/mL. In UC the apparent molecular weight is proportional to the ratio of fringe displacement to concentration. For low enough concentrations this ratio is expected to be constant and proportional to the actual molecular weight. These ratios are 45 mL/g for the 0.002 g/mL and 30.8 mL/g for the 0.006 g/mL concentration. Results from the equilibrium sedimentation of the 0.002 g/mL solution sample yielded an apparent weight average molecular weight of $28.3 \times 10^3 \text{ g mole}^{-1}$. Results from the equilibrium sedimentation of the 0.006 g/mL solution sample yielded an apparent weight average molecular weight of $17.9 \times 10^3 \text{ g mole}^{-1}$.

There may be a variety of possible causes of the observed large apparent molecular weight variation. The molecules may associate in dilute solution. They may have an exceptionally large second virial coefficient. We may be degrading the polymer in DMAC solution during our 300 hour runs in the UC. Finally there may be uncontrolled contamination, most likely by water, in the sample preparation, or during the experiment.

The synthetic boundary measurement is used to determine the refractive index increment between solvent and polymer solution in terms of the number of fringes arising from the Rayleigh optics of the ultracentrifuge. The synthetic boundary measurements were made on the

solutions used for the equilibrium UC runs. The fringe displacements from the synthetic boundary measurements are proportional to be product of concentration and the dn/dc of the solution. Since water has a refractive index very different from the solvent, these measurements are sensitive to uncontrolled water pickup . Synthetic boundary runs on these solutions gave 15.8 mL/g and 14.6 mL/g for the ratio of the fringe displacement to the concentration. This is a difference of about 7%. This difference is beyond what one expects from this measurement. This result seems to indicate we have not eliminated water pickup. We have taken precautions in making the solutions to keep them dry. Thus, the water must be picked up during the loading of the UC cells, or the running of the UC itself. This error, although serious, is much too small to account for the 50% variation in the apparent molecular weight we have seen in the equilibrium UC.

Other causes of the 50% apparent molecular weight variation were investigated. In the next section, we describe an examination by SEC of the degradation of the SRM 1480 in DMAC.

5.0 SEC on Low Molecular Weight Standard, SRM 1480.

Since this polyurethane was designed to be used as a SEC standard it is important that its behavior be normal in the SEC environment. If its behavior is unusual we need to find the conditions under which it becomes normal. Without controlling this behavior, SRM 1480 would become a useless SEC calibrant.

Furthermore, because of problems found in the ultracentrifugation study, we wished to examine the degradation in DMAC using the SEC to monitor the molecular weight changes in degradation experiments over a number of weeks. However as we started the degradation study we found that the shape of the SEC curve and the peak position in the SEC of the polyurethane changed as a function of concentration in THF. Since any possible conclusions obtained from the degradation studies would be in question due to this problem we began studies of the concentration dependence of these polyurethane peaks.

In all the following discussion on SEC studies a Waters 150-C ALC/GPC Liquid Chromatograph with a refractive index (RI) detector was used. Unless otherwise specified Mallinckrodt THF was used as the solvent and two Polymer Labs PL-gel 10 μ m Mixed Bed columns were used.

5.1 Concentration Studies

Early studies on the concentration effect of the SEC of SRM 1480 showed that at fixed injection volume the leading edge of the SEC peak varied with concentration, changing from an elution volume of 15.98 mL for 0.002 g/mL, to 16.18mL for 0.0005 g/mL, to 16.4 mL for 0.00025 g/mL. During all of these runs, the peak position remained at 16.6 mL and the following edges for all concentrations were constant. See figure 4a for an example of this data. At the same time Polystyrene (PS) of molecular weight (M_w) 36,950 was run at concentrations of 0.0005 g/mL to 0.00002

g/mL. This polymer had an elution volume in the same range as SRM 1480. The PS chromatograms showed random peak shifts of less than 0.07 mL. This shift is about the error expected from the data collection rate used at that time, and smaller than the edge shifts observed on the SRM 1480.

Although we felt that the changing of the leading edge could not be a column loading effect, particularly at these low concentrations, we nonetheless decided to check out column loading problems. Concentrations of 0.002 to 0.000125 g/mL of SRM 1480 in THF were run in the SEC with the injection volumes varying in such a manner that the total mass of polymer being separated on the column was always constant. In this case the entire elution volume curves arising from this run were shifted, not just the leading edge. The data, shown in figure 4b, showed peak shifts as a function of concentration. The peak width at half height for the 0.001 g/mL concentration was 1.16 mL while that for the 0.00025 g/mL was 1.25 mL, less than 0.1 mL different. This behavior is not similar to normal column loading effects. Normally column loading is expected to increase peak width at higher concentrations [3].

We were concerned that a small amount of water in the THF might be affecting the association or the size of SRM 1480 in the THF solutions. Since water content was variable in THF used in SEC and hard to control at the level found in the normal SEC solvents, we decided to run the SEC on SRM 1480 with a well defined amount of water in THF to see the effect of high water concentrations. We doped the THF with 1% water. This work led to very inconsistent and irreproducible results. In one series of runs we found no concentration dependence of the peak position, and in another series under what we thought were the same conditions we obtained large variations of the peak position as a function of concentration. What was causing this change was never clear and we were thus unable to control the peak positions or peak widths as a function of concentration of polymer. No consistent pattern was found. Changing the columns to those of a different manufacturer did not change the inconsistency of the results. This line of study was then dropped.

A number of studies of polyurethanes have suggested that the addition of salts to the solvents DMF or DMAC improved the SEC [4]. None of the earlier studies described the concentration effects we found. Rather they found that salts like LiBr in DMF seemed to improve the shape of the SEC curves. Use of salts in THF as a SEC solvent has been reported, but these reports are not concerned with polyurethanes [5].

We have run SEC studies with 0.01 M LiBr in THF. Concentrations of SRM 1480 from 0.002g/mL to 0.0005g/mL in THF with 0.01 M LiBr solutions were run. These solutions gave SEC curves which superimpose on each other showing no shape or peak position dependence on concentration in THF with 0.01 M LiBr. Figure 5 shows an example of our data using this solvent. We therefore will suggest that SRM 1480 be used as a standard reference material in the calibration of SEC columns only when it is used in THF with 0.01 M LiBr added.

5.2 Degradation Under Light

During the equilibrium UC experiment the polymer is exposed to intense green light to record the concentration profile in the UC. The polymer is exposed to about a half an hour of the light during a normal 300 hour UC run. We have exposed solutions of SRM 1480 in DMAC at a concentration of 0.006 g/mL to this green light for 10, 20 and 40 minutes and then run the SEC on the exposed and unexposed samples. The SEC show no effect of exposure to light.

5.3 Degradation in DMAC and THF in the Dark

Degradation studies at 0.006 g/mL concentration in DMAC and THF were run for a period of a month. Solutions were stored in the dark at room temperature. At various times samples were withdrawn and diluted 1/10 in THF. For the solutions in DMAC the 1/10 dilution in THF was enough to move the DMAC peak far from the main polymer peak so that it does not overlap with the polymer peak on the SEC chromatogram. In fact, the initial duplicate runs of the aging experiment for the zero time for the DMAC degrading solution and for the THF degrading solution gave identical PU peaks in the SEC.

For the DMAC degradation runs during the period 8-23-89 to 9-1-89 there was no change in the molecular weight of the polymer. What change we see in the chromatograms can be attributed to the change in the SEC chromatograms themselves since the BHT and water peaks shift about as much as the SRM 1480 peaks. Only for the last run on 9-1-89 is there any indication that this peak has shifted more than either the water or BHT peak.

5.4 Apparent Polystyrene Molecular Weight from SEC

The SEC was run on SRM 1480 as described in section 5.0 and 5.1 with 0.01 LiBr in THF. The columns were calibrated with polystyrene fractions from an Easi-cal tab from Polymer Labs and with SRM 1478 and SRM 1479. We found that the calibration of the SEC by polystyrene in THF, with and without 0.01 M LiBr, was the same within the error of the data collection.

From these calibrations we estimated the polystyrene equivalent molecular weights $(M_i)_{ap}$ of SRM 1480 as

$$\begin{aligned}(M_n)_{ap} &= 25,600 \text{ g mole}^{-1} \\ (M_w)_{ap} &= 60,100 \text{ g mole}^{-1} \\ (M_z)_{ap} &= 104,000 \text{ g mole}^{-1}\end{aligned}$$

6.0 Determination of Molecular Weight of SRM 1480 by Light Scattering

6.1 Estimation of Degradation Rate by Light Scattering

Since we may have had problems with the possible degradation of polyurethane SRM 1480 when it was studied by ultracentrifugation we

proposed to check to see that the materials did not degrade during the course of the light scattering experiment.

By their nature light scattering experiments are short. A number of solutions can be made up and run by light scattering in a single day. To check for degradation, several solutions were made up and run a number of times during one day. They were then stored in the dark and run two days later, four days later, and a week later. The apparent molecular weights of these solution were found to change by less than 5% after standing 12 hours and by less than 15% after standing a week.

As long as we make our solutions up fresh and run them within a day or two, we expect no problem. This was our practice during the entire series of light scattering experiments.

6.2 Light scattering on the Low Molecular Weight Polyurethane Standard

6.2.1 Solution and Solvent preparation

Burdick and Jackson dimethyl acetamide (DMAC) was used as the solvent. Since DMAC is hygroscopic, care was taken to open the solvent bottle in a dry box and to do as much of the sample preparation as possible in the dry box.

Polar solvents such as water are very difficult to make dust free for light scattering measurements. It was found that the DMAC has a great proclivity to hold dust, also.

Before each use, the light scattering cells were cleaned in a xylene vapor chamber in which the condensing vapors removed the dust from the surface of the cells. Filtering with a single 0.22 micron filter was unsuccessful in cleaning the dust out of the solution when the filtration was done in the dry box. We felt that dust was stirred up in the dry box by the cyclic transfer of dry N_2 in and out of the entrance lock of the dry box during the transfer process. This dust was felt to find its way into the filters and solutions. To avoid this problem, solutions were made up in the dry box and filtration was done very quickly outside the dry box. Filtration of solvent and solution usually occurs in less than 15 seconds in the open air. To test that filtration outside the dry box did not change the light scattering signal, scattering at 90 degrees was measured on solvents on which filtering had been done in times as short as 5 seconds and as long as 15 seconds. The scattering signal from these experiments showed no dependence on time of filtration. Thus we are confident that the rapid filtering outside the dry box did not change the solution or solvent properties enough to be measured and thus should not effect the molecular weight value determined.

6.2.2 Determination of dn/dc

The differential refractive index for SRM 1480 in DMAC at 30°C for light of wavelength 633 nm was determined using a LDC/Milton Roy Chromatix KMX-16. The KMX-16 has been calibrated against aqueous NaCl

solutions following the data of Kruis [6]. Solutions of polyurethane prepared for the light scattering experiments were run within a day or so in the KMX-16 to obtain the Δn . A linear least squares analysis of the Δn versus the concentration was carried out. The slope gave a dn/dc of 0.0841 mL/g with a standard deviation of 0.0051 mL/g. The data are shown in figure 6.

6.2.3 Light Scattering Methods

Light scattering measurements on the polyurethane solutions in DMAC were made on a Brookhaven Instruments Model BI-200 light scattering apparatus. A 5 milliwatt He-Ne laser was used as a light source. The laser beam is vertically polarized and a vertical polarizer was used in the detector optics so we have V_v polarization for the scattered intensity. During any one day 3 or 4 solutions were made up, filtered into the light scattering cells which had teflon lined screw caps on them, and run. Often the solutions were kept in the dark overnight and run for a second time early the next day with little apparent change in the molecular weight.

6.3 Analysis of Light Scattering Data

Light scattering data at V_v polarization from polymer solutions of concentrations c at scattering angles θ may be analyzed by fitting $I(\theta, c)$, the scattering signal from a solution of concentration c at scattering angle θ to

$$I(\theta, c) = I(\theta, 0) + c I_G / \left((\sin \theta) \sum_{ij} C_{ij} c^i \sin^{2j}(\theta/2) \right). \quad (1)$$

In eqn (1) I_G is the scattering signal from the benzene working standard at $\theta = 90^\circ$.

In order to use eqn (1) for the estimation of molecular parameters, we must first decide how many terms on the right-hand side must be included to provide an adequate fit to the experimental data. The dependence of c/I_c , where $I_c = \sin\theta [I(\theta, c) - I(\theta, 0)]/I_G$, upon c and upon $\sin^2(\theta/2)$ reflects solute-solvent interactions and solute size, respectively. Accordingly, preliminary scattering data for SRM 1480 were first analyzed as c/I_c versus $\sin^2(\theta/2)$ at constant concentration and versus c at constant scattering angle, to see whether a linear expansion (i.e., retaining only C_{00} , C_{01} , and C_{10}) would provide an adequate fit. The analysis revealed that the linear approximation was adequate at concentrations below 0.014 g/mL. The next higher order terms, C_{20} and C_{02} , were included in the final fit to show that the data were consistent with this hypothesis.

Thus we used for the final analysis

$$I(\theta, c) = I(\theta, 0) + c I_G / \left(\sin \theta (C_{00} + C_{01} \sin^2(\theta/2) + C_{10} c + C_{11} c \sin^2(\theta/2) + C_{20} c^2 + C_{02} (\sin^2(\theta/2))^2) \right) \quad (2)$$

The coefficients in eqn (2) are related to the weight-average molecular weight M_w , molecular mean-square radius of gyration R_G^2 , and second and third virial coefficients, A_2 and A_3 , by [7]:

$$M_w = (K' C_{00})^{-1} \quad (3)$$

$$R_G^2 = 3[\lambda_0 / (4\pi n)]^2 C_{01} / C_{00} \quad (4)$$

$$A_2 = 1/2 K' C_{10} \quad (5)$$

$$A_3 = 1/3 K' C_{20} \quad (6)$$

$$K' = 4\pi^2 n_B^2 (dn/dc)^2 / (\lambda_0^4 N_A V_v^B) \quad (7)$$

where:

λ_0 is the wavelength in vacuum of the scattered light, 632.8 nm in this work, n and n_B are the indices of refraction of the solvent and benzene taken as 1.435 [8] and 1.503 [7], respectively, dn/dc is the differential refractive index of the solution, measured as described in 6.2.2, N_A is Avogadro's number, taken as $6.022 \times 10^{23} \text{ mol}^{-1}$, V_v^B is the Rayleigh ratio for the vertically polarized scattering of vertically polarized light from benzene, used for calibration and obtained as described in the following paragraph.

The "vertical-vertical" Rayleigh ratio V_v is related to the Rayleigh ratio R_v for the unpolarized scattering of vertically polarized He-Ne laser and the depolarization ratio p_v for polarized light by:

$$V_v^B = R_v^B / (1 + p_v) \quad (8)$$

Using the published [10] values for benzene

$$R_v^B = 12.6 \times 10^{-6} \text{ cm}^{-1}$$

and $p_v = 0.265$, we obtain

$$V_v = 9.96 \times 10^{-6} \text{ cm}^{-1}$$

6.4 Results

Eight independent sets of light scattering runs were made on SRM 1480 using DMAC as a solvent. Two sets were discarded because the highest concentration in the run indicated a large contribution from A_3 . One set at very low concentration was discarded due to the very small signal over solvent scattering at the lowest concentrations.

Each of the five remaining sets consisted of scattering measurements on the four solutions, together with solvent measurements, for at least seven scattering angles. The scattered intensities in each set were fitted by least squares to eqn (2), and the results were used to calculate M_w , A_2 and A_3 using eqns (3)-(7). No estimate was made of R_G^2 at these low

molecular weights. The values of M_w , A_2 , and A_3 obtained from the five sets were then averaged. The resulting mean values and sample standard deviations are given in table 2. We see that light scattering gave a weight average molecular weight of about 4.7×10^4 g mole⁻¹ with an standard deviation of 3.3×10^4 g mole⁻¹ and a value of A_2 of 0.00130 mol cm³/g².

From the data in table 2 the average value of the A_3 is less than its standard deviation. This suggests that A_3 is not significant in this measurement. Furthermore, if A_3 were to contribute significantly to the extrapolation to zero concentration scattering to obtain the molecular weight, then $1.5 A_3 c_m$, where c_m is the maximum concentration used in the fitting scheme, would have a value on the order of A_2 . If we use the average value of A_3 from table 2, this product is two orders below A_2 . If we use the maximum value of A_3 found in table 2 this product is less than the standard deviation in A_2 . Finally, the Zimm plot of one set of data, Figure 7, shows no curvature in the concentration at fixed angle plots. This too indicates there is negligible contribution for A_3 . Thus we are confident A_3 makes no significant contribution in this concentration range to the extrapolation of the light scattering to zero concentration.

7.0 Conclusions

The weight average molecular weight of SRM 1480, a model polyurethane, was determined to be 4.7×10^4 g mole⁻¹. The intrinsic viscosity of SRM 1480 in THF was found to be 43.8 mL/g.

The SEC of SRM 1480 in THF as received in the bottle exhibited concentration dependent peak positions even for low concentrations. The addition of 0.01 moles per liter LiBr to the THF was found to alleviate this problem. This low concentration of LiBr did not however change the PS calibration of the SEC columns.

Table 1 Viscosity Number as a Function of Concentration of SRM 1480

(THF at 30 °C) Concentration g/mL	Viscosity No. mL/g
0.005004	48.10
0.007504	50.01
0.007505	49.96
0.002502	45.54
0.005003	48.04
0.002501	45.69
<hr/>	
Results of fit	
Limiting Viscosity number	43.80
Standard Deviation	0.17

TABLE 2

Molecular Weight, A_2 and A_3 for SRM 1480

Run Label	$M_w \times 10^{-3}$ g/mol	A_2 cm^3/g^2	A_3 cm^6/g^3
LS1129	46.8	0.00128	0.0057
LS1128	48.7	0.00138	-0.003
LT12456	52.0	0.00197	-0.069
LT125D6	44.0	0.00098	0.045
LU1121A	44.7	0.00087	0.047
Average	47.3	0.00130	0.0051
Standard Deviation	3.3	0.00043	0.047

References

- [1] Cannon, Manning, and Bell, Anal. Chem, 32, 355-358(1960)
- [2] Richards, Teller, and Schachman, Biochem. J 1054-76 (1968)
- [3] G. Glocker, "Polymer Characterization by Liquid Chromatography," Journal of Chromatography Library - Vol. 34, Elsevier, Amsterdam, 1987, Pg 377 and following.
- [4] N.D. Hann, J Polymer Sci A-1, Polymer Chem. 6, 1331-1339
- [5] G. Glocker, "Polymer Characterization by Liquid Chromatography," Journal of Chromatography Library - Vol. 34, Elsevier, Amsterdam, 1987, Pg 390 and following.
- [6] A. Kruis, Z. Physik. Chec. B 34, 13 (1936).
- [7] See, for example, Han, Verdier and Wagner, J. Res. NBS 83, 185-193 (1978).
- [8] J. A. Riddick and W. B. Bunger, "Organic Solvents," Wiley Interscience, pg 450, New York, 1970.
- [9] W. Kaye and J. B. McDaniel, Applied Optics, 13, 1934 (1974).

Captions

Figure 1. Homogeneity testing of first bottling using SEC. Sample used in runs A and B are from same bottle as are runs C and D. Runs A and B show within bottle variation of the MWD while C and D show no within bottle variation. The difference between A-B and C-D shows the significant bottle to bottle variation we see. Both axis are in arbitrary units.

Figure 2. Homogeneity testing after second bottling of SRM 1480 using SEC. SEC of samples from four different bottles show no bottle to bottle variation. No within bottle variation was found either. This result is to be compared with figure 1.

Figure 3. Plot of viscosity number versus concentration for SRM 1480 in THF.

Figure 4a. Effect of concentration variation of SRM 1480 in "as received" THF for concentration from 0.001g/mL to 0.0001g/mL. The left most peak is 0.001g/mL of SRM 1480 in THF and the right most peak is the signal for 0.0001g/mL. RI signals on all SEC are normalized so that maximum of peak at each concentration is 1.0 for ease of seeing distribution and peak movement. (SEC columns are different from those used in figures 1 and 2.)

Figure 4b. Effect of column loading on SEC of SRM 1480 in "as received" THF for concentration from 0.002g/mL to 0.00012g/mL. The left most peak is 0.002g/mL of SRM 1480 in THF and the right most peak is the signal for 0.00012g/mL. RI signals on all SEC are normalized so that maximum of peak at each concentration is 1.0 for ease of seeing distribution and peak movement.

Figure 5. Little or no concentration variation of the peak position is seen with the addition of 0.01m LiBr to the THF. This is to be compared to figure 4 above. Concentration range is from 0.001g/mL to 0.000125g/mL of SRM 1480.

Figure 6. Plot of change in refractive index from solution to solvent as a function of concentration for SRM 1480 in DMAC. The slope of this line is (dn/dc) .

Figure 7. Example of Zimm plot for one of the runs of SRM 1480. Lines are calculated values and points are experimental data.

Figure 1

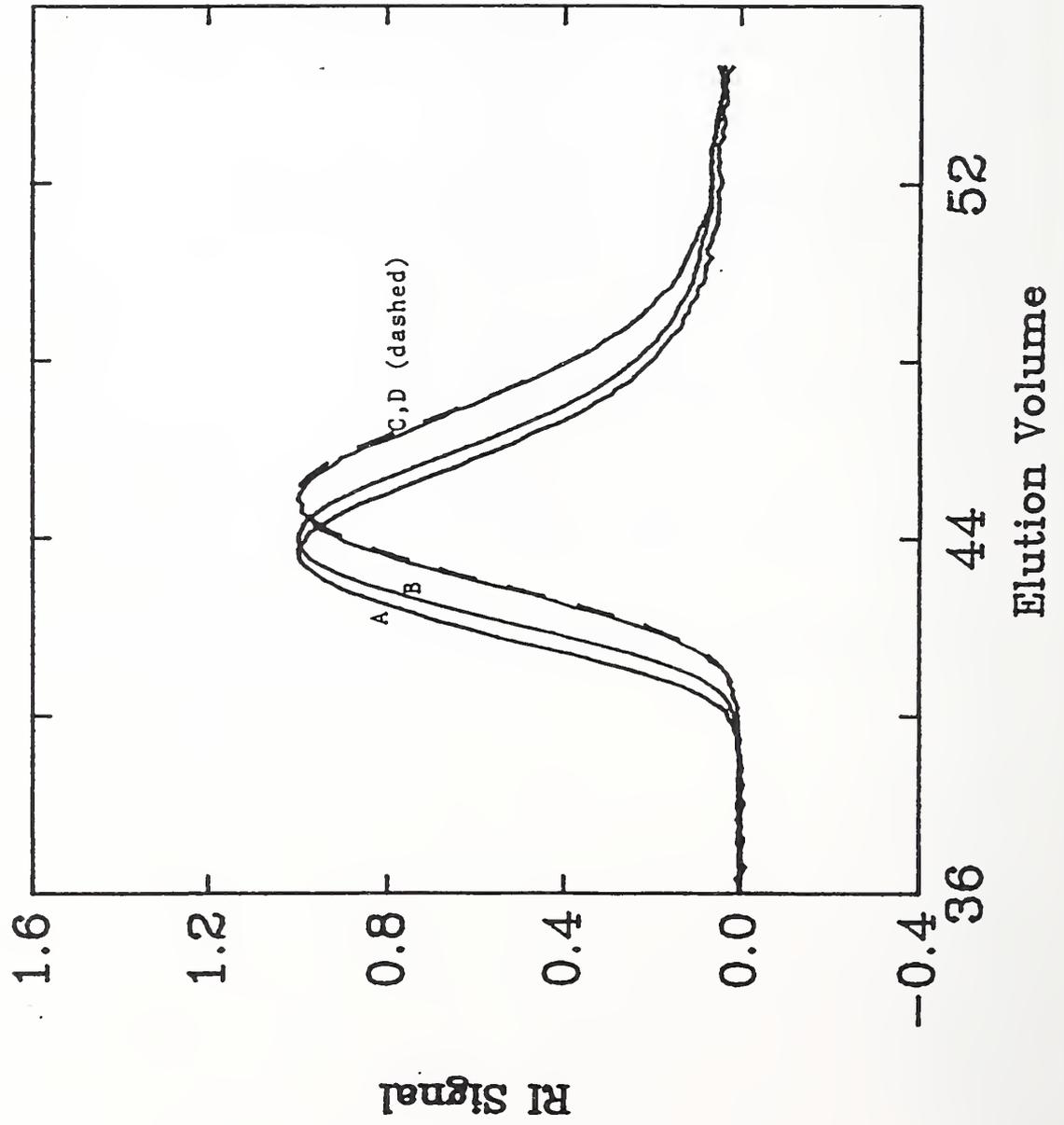


Figure 2

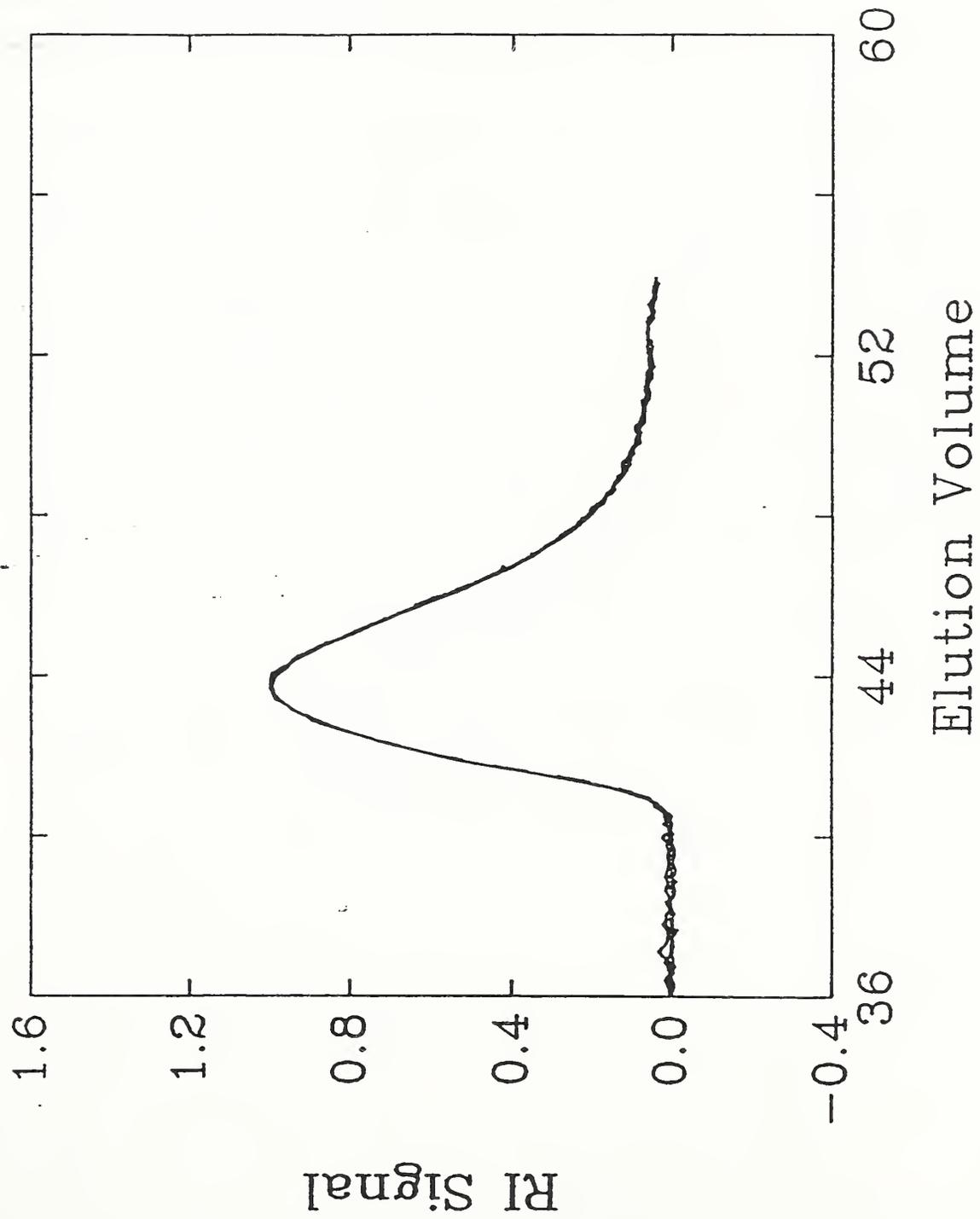
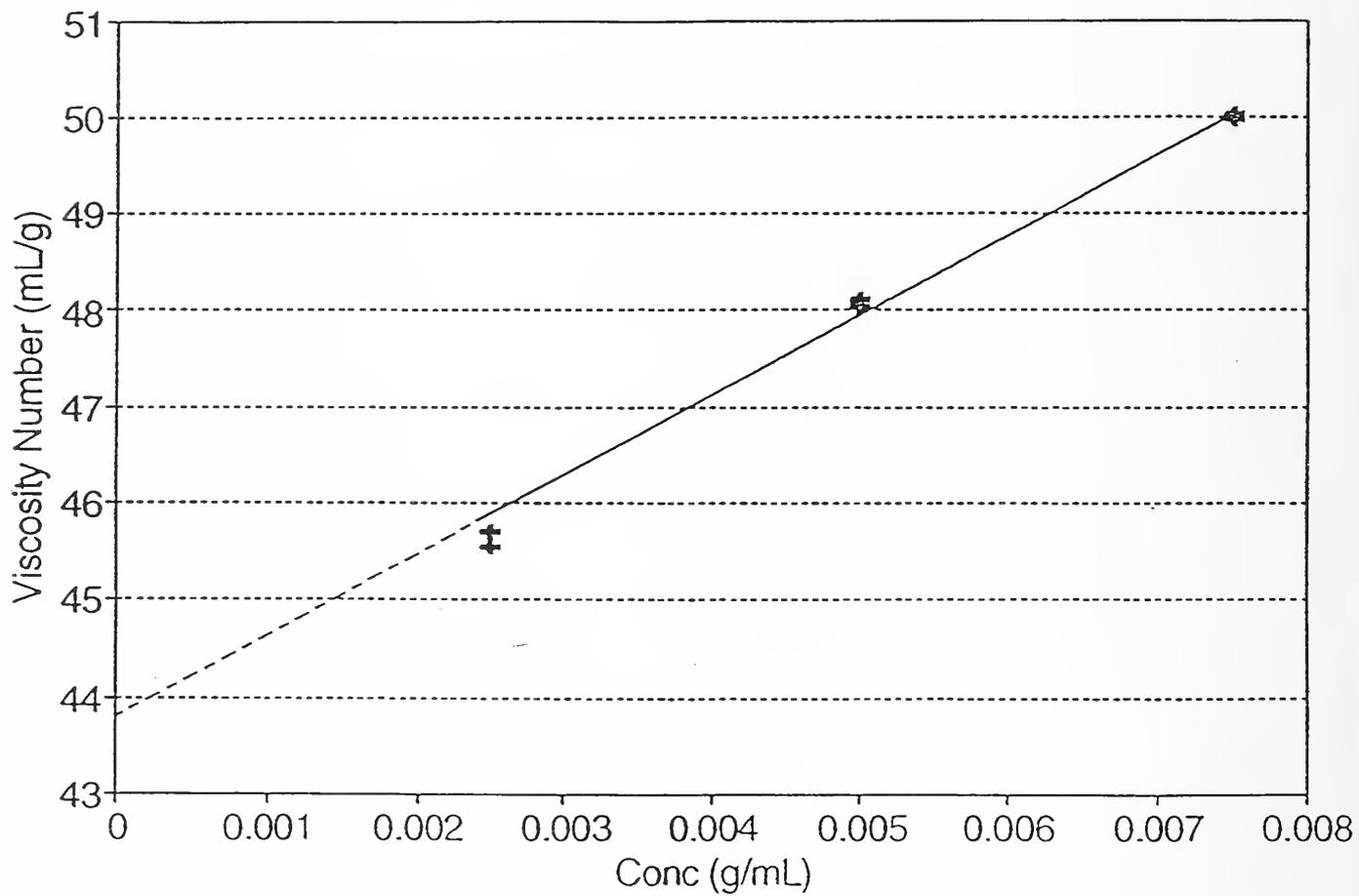
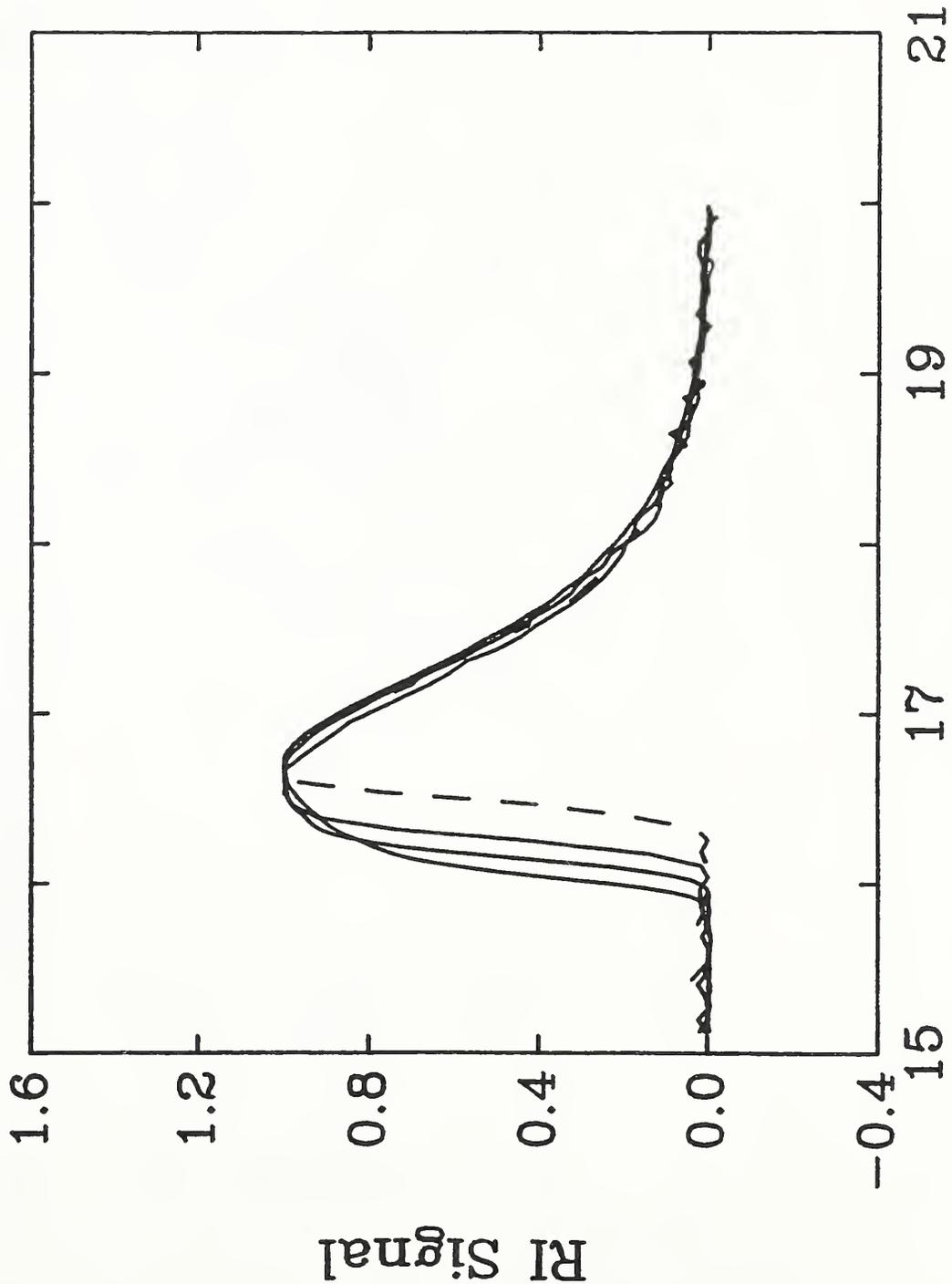


Figure 3

Intrinsic Viscosity of SRM 1480





Elution Volume

Figure 4b

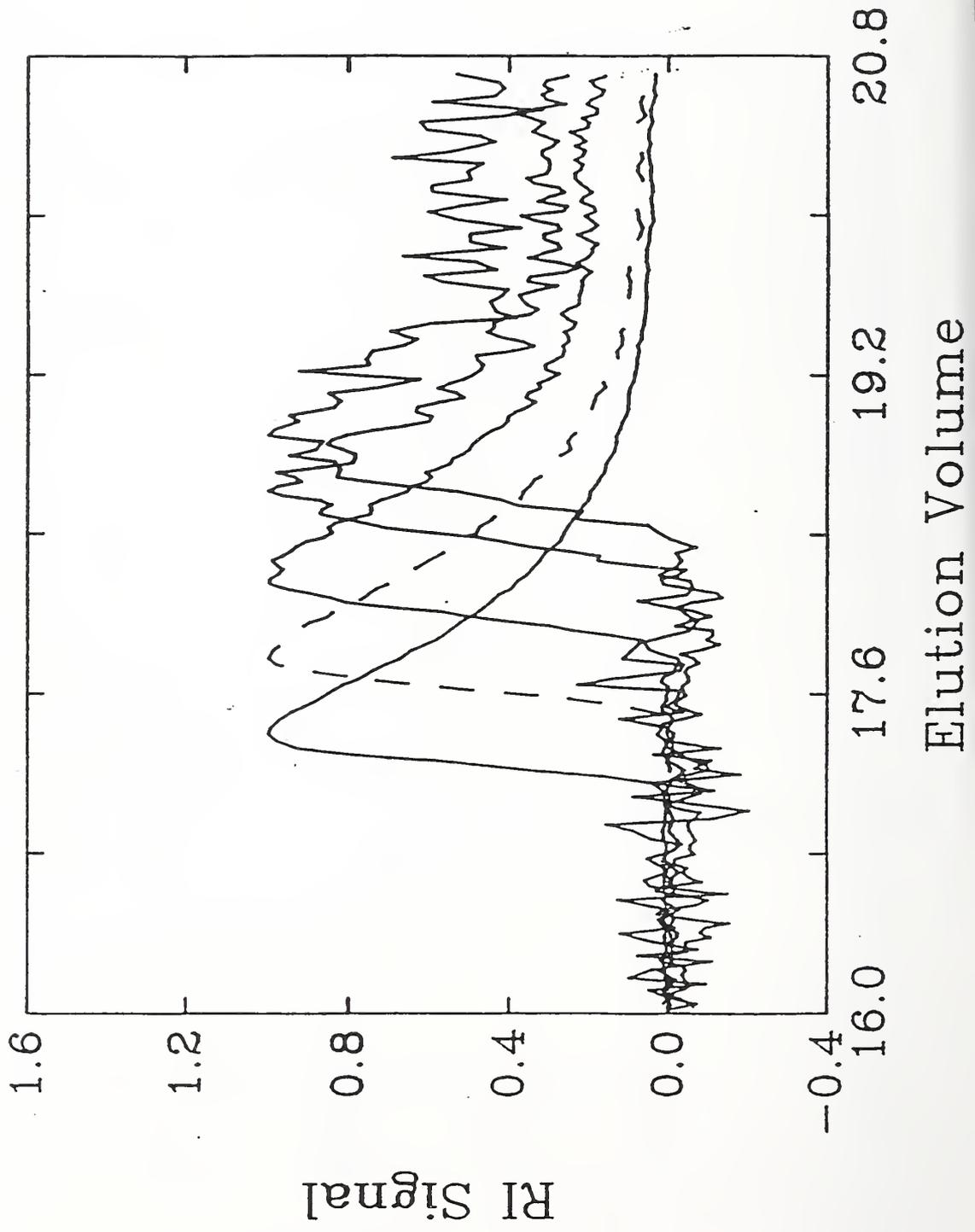


Figure 5

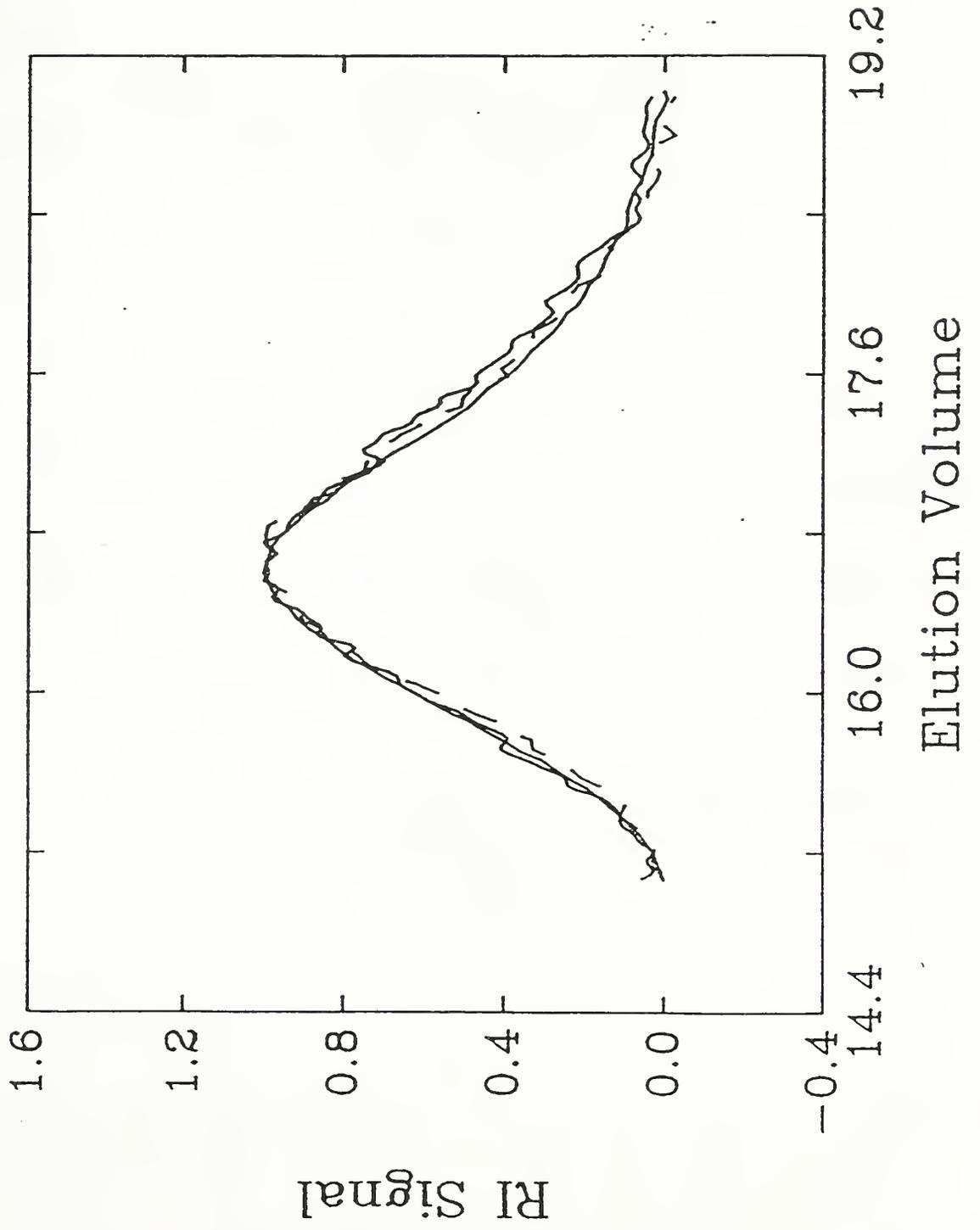


FIG 6

Determination of dn/dc for SRM 1480 in DMAC

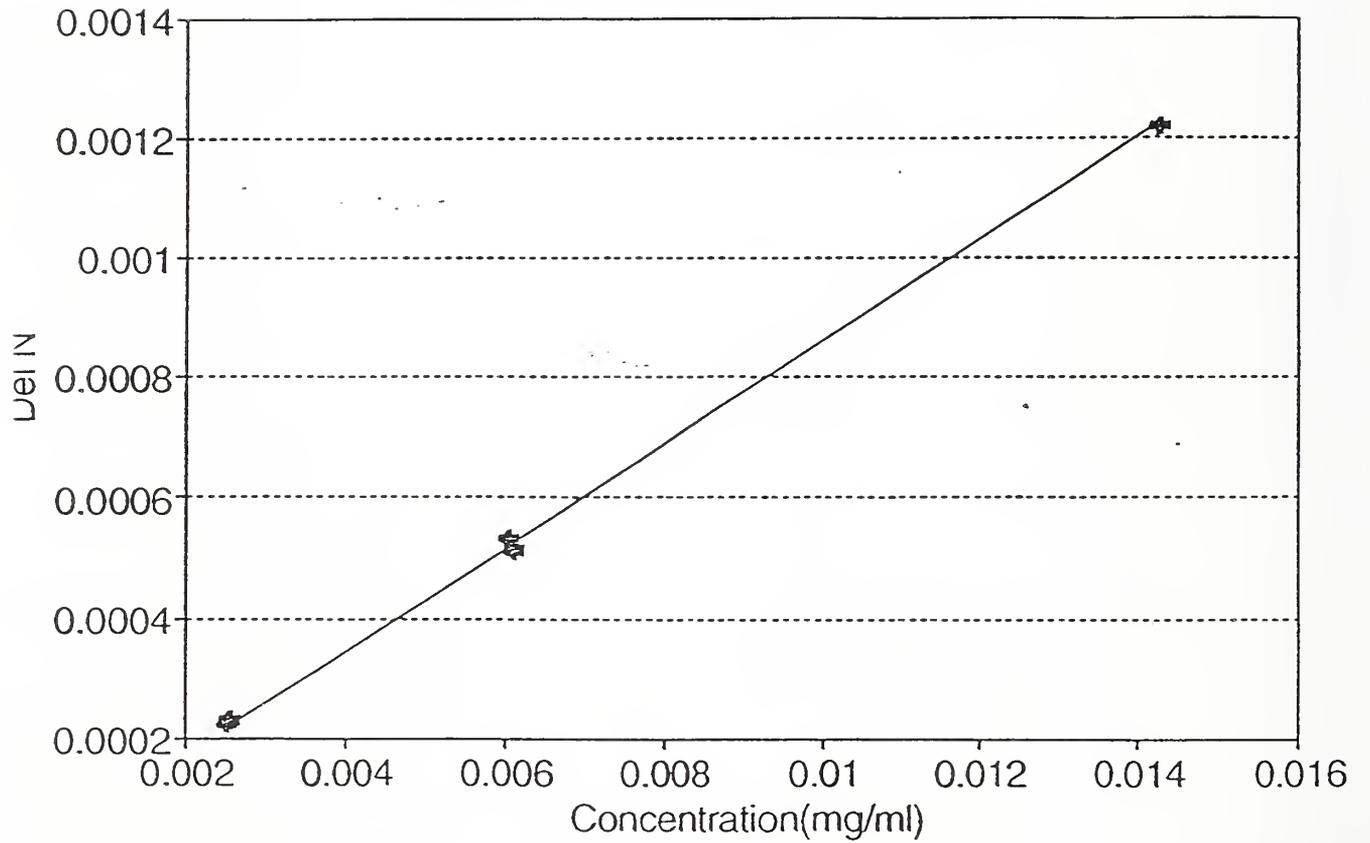
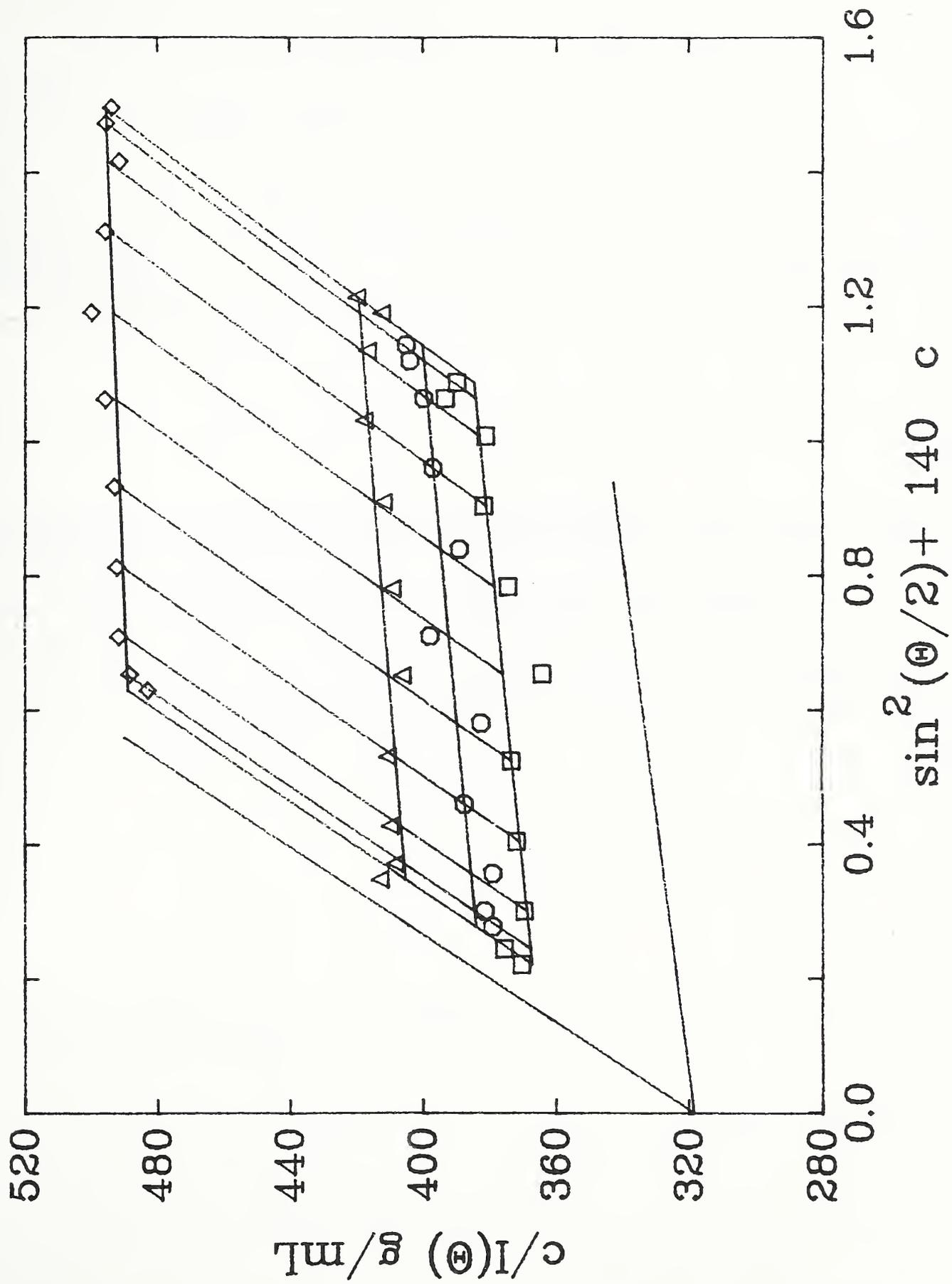


Figure 1



NIST-114A
(REV. 3-89)

U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY

BIBLIOGRAPHIC DATA SHEET

1. PUBLICATION OR REPORT NUMBER
NISTIR 4788

2. PERFORMING ORGANIZATION REPORT NUMBER

3. PUBLICATION DATE
April 1992

4. TITLE AND SUBTITLE

Development of Characterization Techniques for Polyurethanes I. Characterization of SRM 1480 A Low Molecular Weight Polyurethane for SEC Calibration

5. AUTHOR(S)

C.M. Guttman, J. R. Maurey, P.H. Verdier, C. C. Han, F. W. Wang

6. PERFORMING ORGANIZATION (IF JOINT OR OTHER THAN NIST, SEE INSTRUCTIONS)

U.S. DEPARTMENT OF COMMERCE
NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
GAITHERSBURG, MD 20899

7. CONTRACT/GRANT NUMBER

8. TYPE OF REPORT AND PERIOD COVERED

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (STREET, CITY, STATE, ZIP)

10. SUPPLEMENTARY NOTES

DOCUMENT DESCRIBES A COMPUTER PROGRAM; SF-185, FIPS SOFTWARE SUMMARY, IS ATTACHED.

11. ABSTRACT (A 200-WORD OR LESS FACTUAL SUMMARY OF MOST SIGNIFICANT INFORMATION. IF DOCUMENT INCLUDES A SIGNIFICANT BIBLIOGRAPHY OR LITERATURE SURVEY, MENTION IT HERE.)

The characterization of a polyurethane standard reference material, SRM 1480, is described. The weight average molecular weight of SRM 1480 by light scattering was determined to be about 5×10^4 g mole⁻¹. The intrinsic viscosity of SRM 1480 in THF was also measured.

The SEC of SRM 1480 in THF as received in the bottle was found concentration dependent peak positions even for low concentrations. The addition of 0.05 moles per liter LiBr to the THF was found to alleviate this problem. This low concentration of LiBr did not however change the PS calibration of the SEC columns.

12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

calibration, intrinsic viscosity, molecular weight standard, polyurethane, standard reference material, size exclusion chromatography

13. AVAILABILITY

UNLIMITED
 FOR OFFICIAL DISTRIBUTION. DO NOT RELEASE TO NATIONAL TECHNICAL INFORMATION SERVICE (NTIS).
 ORDER FROM SUPERINTENDENT OF DOCUMENTS, U.S. GOVERNMENT PRINTING OFFICE, WASHINGTON, DC 20402.
 ORDER FROM NATIONAL TECHNICAL INFORMATION SERVICE (NTIS), SPRINGFIELD, VA 22161.

14. NUMBER OF PRINTED PAGES

27

15. PRICE

A03

